EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) ACCUMULATION IN PLANTS

THE POTENTIAL USE OF PAH ACCUMULATION AS A MARKER OF EXPOSURE TO AIR EMISSIONS FROM OIL AND GAS FLARES

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Prepared for:

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August 2000

Pub. No. T/558
ISBN: 0-7785-1228-2 (Printed Version)
ISBN: 0-7785-1229-0 (On-Line Version)
Web Site: http://www.gov.ab.ca/env/

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This report may be cited as:

Slaski, J.J., Archambault, D.J., Li, X., 2000. Evaluation of polycyclic aromatic hydrocarbon (PAH) accumulation in plants. The potential use of PAH accumulation as a marker of exposure to air emissions from oil and gas flares. ISBN 0-7785-1228-2. Report prepared for the Air Research Users Group, Alberta Environment, Edmonton, Alberta.

FOREWORD

Oil and gas flare emissions have been the subject of recent scientific investigation and public interest. Efforts to address the issue have been conducted on several fronts, including reductions in the number of flares in the province, reductions in volumes of gas flared, measurement of the types and amounts of compounds released from flares, and measurement of the environmental effects of flare emissions.

Polycyclic aromatic hydrocarbons (PAHs) are a class of complex substances that are produced during incomplete combustion of fossil fuels. PAHs are one component of air emissions from oil and gas flares. Although PAHs and other substances released from flares may have environmental effects, it is very difficult to determine the extent of exposure of vegetation to flare emissions, and therefore, it is difficult to measure any effects of these emissions. Due to variability inherent in any weather pattern (wind speed, wind direction, humidity, temperature, etc.), exposure of vegetation to emissions from a flare is sporadic; only when the wind speed and direction cause emissions to impinge upon a plant does exposure occur. Exposure to other stresses, and possible responses to these stresses, must be considered in an exposure assessment to ensure that any observed effect is due to the exposure to the flare emission and not to another emission source or other environmental stress.

There are two means of determining if exposure has occurred. First, ambient air quality monitoring technology can be installed near the plants or trees in the vicinity of a flare. Continuous monitoring methods are expensive, requiring an investment in the monitoring or sampling instruments, and in a power supply to operate the monitors or samplers. Passive monitors are also available and are less expensive, but the range of substances for which these monitors are available is limited. The data obtained from passive monitors has other limitations, the most significant being that they can only provide an estimate of the concentration of substances in the air averaged over long time periods (several weeks to months).

The second means of determining if exposure has occurred is through the use of vegetation itself. Some of the substances released from combustion within a flare may chemically adhere to leaves or branches, thereby "marking" that plant as one that has been exposed. Some substances are also incorporated into the leaf and are incorporated into the biochemical processes that operate naturally within plants and trees. Substances that have been so metabolized may also "mark" the tree or shrub as having been exposed to flare emissions.

The Air Research Users Group of Alberta Environment commissioned this review of the scientific literature of PAH accumulation within plant material that occurs following exposure to air containing PAHs. The conclusions of this review will contribute to a decision on whether or not to pursue a field investigation into the use of PAH accumulation in plant parts as a marker of exposure of the plants to emissions from oil and gas flares.

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EXECUTIVE SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) are a family of 660 chemical compounds with a molecular structure consisting of at least two fused aromatic (benzene) rings. They are predominantly formed as a result of the incomplete combustion of organic fuels. Although natural sources of emissions such as forest fires and volcanic eruptions can contribute to background amounts of PAHs in the atmosphere, anthropogenic activities are the primary sources of these compounds. In Alberta, more than 5300 solution gas flares are currently in operation. Concentrations of PAHs in the vicinity of flare operations are comparable to those found in large industrialized cities.

Airborne PAHs can exist in the gas or solid (particle) phase. The phase state of a given PAH is determined by its vapor pressure and the ambient temperature. Water solubility of these non-ionic compounds depends mainly on their chemical structure. The solubility of PAHs in water decreases as their molecular weight increases, while their solubility in lipids increases. Since PAHs possess lipophilic properties, they tend to associate with organic matter containing fatty acids and waxes. Typically, a variety of different PAHs occur together, and their overall properties and effects on the environment vary according to the combination of PAH compounds involved.

Plants are important sinks for atmospheric PAHs, playing a role in the annual cycling of PAHs. Vegetation has been successfully used as a quantitative indicator of exposure to both gaseous and solid phase PAHs in ambient air. Numerous studies have shown that leaves are the main sinks of airborne PAH compounds in plants, while uptake of PAHs from soils via the root system appears to be negligible. The process of accumulation is affected by several abiotic and biotic factors, including vapor-particulate partitioning in the atmosphere, ambient temperature, octanol-air partitioning coefficients, leaf surface area and lipid concentration in plant tissues. Compounds of intermediate volatility are mainly subject to dry gaseous deposition while nonvolatile substances (containing six and more rings) are primarily accumulated on plant surfaces in the form of dry, particle-bound deposits. The partitioning of PAHs between the atmosphere and vegetation depends on ambient temperature. As air temperatures decrease in fall and winter, conifer and evergreen plants scavenge the majority of emitted PAHs. At high ambient temperatures in summer, low molecular weight compounds can revolatilize to the atmosphere. The most important anatomical feature of plants that affects the rate of interception and accumulation of airborne PAHs is total leaf area. Volatile PAHs enter plants primarily through gaseous diffusion via open stomata, although absorption by the waxy leaf surface accounts for a portion of total PAHs in tissues. The waxy surface of leaves intercepts both particulate and vapor phase contaminants.

A wide variety of plant species have been used as indicators to evaluate PAH contamination levels in cities and heavily polluted industrial regions as well as for the identification of unknown points of emission. Two basic strategies can be employed in biomonitoring studies: active and passive monitoring.

Active monitoring refers to a process by which plants are grown in an artificial environment without previous contact with a pollutant of interest and plants are subsequently transferred to a

monitoring site and exposed to ambient air over a given period of time before being returned to the laboratory for analysis. It has been documented that active air monitoring with a network of moss bags placed in the area of interest can facilitate evaluation of PAH distribution over time and space and can be used to identify point sources of PAHs. Mosses are particularly useful for monitoring purposes due to their large surface area, high capacity to absorb large organic molecules and their abilities to obtain water and nutrients from the air.

Passive monitoring relies on the analysis of pollutant content in plant tissues collected from their natural habitat. Several passive monitoring studies have been conducted to reflect long-term accumulations of persistent trace pollutants such as PAHs. Measurements of PAHs accumulated in plant tissues are taken at various distances from the source, ranging from 0.5 m to 4.5 km.

To the best of our knowledge, no studies on the accumulation of PAHs in plant tissues as markers of exposure to emissions from oil and gas flares have been published in Canada or in any other country. For this reason, all data on accumulation of PAHs in plants presented in this report come from studies of emissions from urban sources (mainly traffic exhaust), various industrial operations and a large-scale industrial fire. These emitters of PAHs generate a pool of similar compounds to those emitted by oil and gas flares, allowing us to draw upon the literature in our consideration of the accumulation of PAHs from oil and gas flares in vegetation and placing it into an Alberta context.

We recommend conducting studies on PAH accumulation in two plant species widely distributed throughout Alberta - lodgepole pine and canola. Additionally, active monitoring by means of moss (Sphagnum fuscum) bags should be used in the comparison of flare emissions from locations surrounded by different types of vegetation or at sites where suitable vegetation is not present. Needles of conifer species should be harvested twice a year in March (over-wintered leaves) and in September (new leaves) to monitor differences in accumulation of PAHs between winter and summer. Leaves of canola should be sampled in July after a 2-month period of interception of air emissions from flares. Exposure of Sphagnum bags for 3 weeks in the vicinity of flare operations would allow a minimum of 5 analyses per vegetation season (May-September). Based on a limited amount of information on plume dispersion and estimated ground level concentrations of PAHs we suggest that in central Alberta plant leaves should be sampled at a distance of 500 m either to the NW or the SE of the flare where annual average ground level concentrations of PAH are predicted to reach their maxima. We also recommend that sampling distances and directions be experimentally verified. Anthracene, pyrene and fluoranthene contents in plant tissues should be analyzed from the area adjacent to sweet gas flaring while phenanthrene, pyrene and fluoranthene contents in plant tissues should be examined from areas surrounding sour gas operations.

ACKNOWLEDGEMENTS

This project was supported by funds from Alberta Environment. The authors thank Dr. Kenneth Foster for his numerous comments and suggestions during the preparation of this report.

101-03740/

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of two or more fused benzene rings. They occur normally in nature primarily as a result of forest fires, however anthropogenic combustion activities and refining processes of fossil fuels are principal sources of these compounds in ambient air. Concentrations of PAHs in air, water and soils have constantly increased over the last 100 years, particularly in industrialized areas (Jones et al. 1989).

Concentrations of PAHs in ambient air have been monitored in several developed countries since the early sixties (Grimmer 1983, US DHHS 1995). Most of these studies were conducted in large municipalities or industrial centers where PAHs are emitted by vehicles, domestic heating, or other combustion of fossil fuels. Traditionally, measurements of PAHs in ambient air have been performed using mechanical samplers equipped with systems for the interception of these compounds in particulate and gaseous phases. In the past decade PAHs have attracted the attention of many researchers throughout the world because of the growing body of evidence showing that plants can be used as quantitative and qualitative indicators of PAH levels in the environment. However, the accumulation of PAHs in plant tissues as a marker of exposure to emissions from oil and gas flares has not been studied. We have focused this review on biotic and abiotic factors affecting accumulation of airborne PAHs in plants and have evaluated the potential use of PAH accumulation in plants as a quantitative marker of exposure to emissions from oil and gas flares in Alberta. To the best of our knowledge this is the first comprehensive review of the literature on this subject.

2. SOURCES OF PAHS

Natural sources of emissions such as prairie and forest fires or volcanic eruptions contribute to the global background of PAHs in the atmosphere. In Canada, forest fires release approximately 2000 tons of PAHs per year and are the single most important natural source of PAHs. However, since releases from this source are generally widely separated in time and space across the country, they do not result in continuous exposure of vegetation in any specific area. Anthropogenic activities such as automobile and furnace exhausts, coal and oil-fired power plants, gasification/liquefaction of fossil fuels, coke and asphalt production, waste incinerators, aluminum smelting and gas and oil flare operations are the primary sources of air borne forms of these compounds. These sources result in emissions of PAHs into all environmental compartments, including soil, vegetation, aquatic bodies and their sediments. In Canada, aluminum smelters are the greatest anthropogenic sources of PAHs released to the atmosphere [925 tons/year (t/yr.)]. Major sources of PAHs to aquatic and terrestrial environments include creosote-treated products (up to 2000 t/yr.), spills of petroleum products (76 t/yr.), metallurgical and coking plants (4 t/yr.) (Environment Canada 1994). In Alberta, the largest supplier of hydrocarbon energy resources in Canada, PAHs are released to the atmosphere by the oil and gas industry (Strosher 1996). More than 5300 solution gas flares are currently in operation in Alberta, burning an estimated 2340×10^6 m^3 produced by the upstream oil and gas industry annually, with numerous PAHs being emitted due to these operations (Table 1, Strosher 1996). Based on Strosher's data, Leahey (1996) calculated the largest ground level concentrations of fifteen PAHs associated with flaring of sweet and sour gases. He found that concentrations of

Table 1. **Polycyclic aromatic hydrocarbons in emissions form flare operations in Alberta. (Adapted from: Strosher 1996).**

a. PAHs identified in emissions from sweet solution gas flame (mg/m^3).

Compound	Amount
NAPHTHALENE	172.64
ACENAPHTHYLENE	139.72
ACENAPHTHENE	60.66
PHENANTHRENE	1.22
ANTHRACENE	74.18
FLUORANTHENE	52.11
PYRENE	83.75
BENZO(C)PHENANTHRENE	17.25
BENZO(GHI)FLUORANTHENE	35.78
CYCLOPENTA(CD)PYRENE	66.10
CHRYSENE	0.30
BENZO(K)FLUORANTHENE	15.97
BENZO(E)PYRENE	1.77
BENZO(A)PYRENE	3.42
PERYLENE	3.56
DIBENZO(DEF,MNO)CHRYSENE	0.75
BENZO(GHI)PERYLENE	1.81
INDENO(1,2,3-CD)PYRENE	4.69
CORONENE	0.12
TRIPHENYLENE	1.47

b. PAHs identified in emissions from the sour oilfield battery flare (mg/m^3).

Compound	Amount
NAPHTHALENE	77.11
ACENAPHTHENE	5.22
PHENANTHRENE	34.09
FLUORANTHENE	14.10
PYRENE	83.26
CYCLOPENTA(CD)PYRENE	9.66
CHRYSENE	2.40
BENZO(A)PYRENE	0.46

some PAHs were comparable to those in large industrialized Canadian cities (Toronto and Montreal). Daily average values reached 1.7 ng/m^3 to 818.9 ng/m^3 for coronene and fluoroethane, respectively.

3. PHYSICO-CHEMICAL PROPERTIES OF PAHS AND THEIR MODIFIED PRODUCTS

Polycyclic aromatic hydrocarbons (PAHs) are a family of chemical compounds with a molecular structure consisting of at least two fused aromatic (benzene) rings in linear, angular or cluster arrangements. By definition they contain carbon and hydrogen atoms although nitrogen, sulfur, chlorine and oxygen may readily substitute into the benzene ring to form heterocyclic aromatic compounds, commonly grouped with the PAHs. The PAH family includes 660 substances indexed by the National Institute of Standards and Technology (Sander and Wise 1997). Approximately 30 to 50 of them commonly occur in the environment (Grimmer 1983, US DHHS 1995). PAHs are formed as a result of incomplete combustion of organic matter through the condensation of ethylenic radicals in the gas phase to form the larger policyclic compounds (Lane 1989, Strosher 1996).

PAHs may be subdivided into two groups based on whether they exist in the gas or solid (particle) phase. The phase state of a given PAH is determined by its vapor pressure and ambient temperature. Compounds with vapor pressures in excess of $1x10^{-5}$ kPa occur predominantly in gas phase, while those with vapor pressures below $1x10^{-9}$ kPa exist exclusively in the particle phase (Bacci et al. 1990). It has been shown experimentally that at 25 °C, three-ringed PAHs were found primarily in the vapor phase (anthracene, phenanthrene), four and five-ringed PAHs were distributed between the particle and vapor phases (pyrene, fluoranthene), while PAHs with six and more rings were found almost exclusively in the particle phase (benzo[a]pyrene, anthanthrene) (Yamasaki et al. 1982). The vapor pressure of PAHs changes by an order of magnitude with incremental changes in temperature of approximately 15 °C. During the hottest days of the year when temperatures approach +40 °C even benzo[a]pyrene has been detected in vapor phase. Decreases in ambient temperatures to –20 °C from +25 °C, resulted in a drop in vapor pressure of three orders of magnitude and many of the lighter PAHs were detected in the particulate phase (Yamasaki et al. 1982). Several studies have shown that PAHs are attached mainly to particles of less than 3 μm in diameter (cit. in Lane 1989). In the absence of wet deposition these small particles may reside in the atmosphere for many days and can be transported from a point source to considerable distances before returning to the earth directly or in rainfall. It has been documented that submicron particles of urban aerosols have atmospheric life-times of up to 40 days, while particles 1-10 μm in size can float in the air for about 100 h (Eswea & Corn 1971).

Another important characteristic of PAHs is their water solubility, which can be described using the octanol-water partitioning coefficient (K_{ow}). Low molecular weight, volatile PAHs with less than four rings are water soluble with a low affinity for particle adsorption ($\log K_{ow} < 5$). PAHs with high molecular weights are generally water insoluble and have a strong affinity for adsorption onto particle surfaces that are suspended in air and water ($\log K_{ow} > 5$). For example, solubility in distilled water at 25 °C varies from 31,690 ppb for the two-ringed naphthalene (log

K_{ow} – 3.29) to 1.8 ppb for the four-ringed chrysene (log K_{ow} – 5.86) (May 1980). Since PAHs possess lipophilic properties, they tend to associate with organic matter containing fatty acids and waxes such as plant membranes and cuticles.

PAHs absorb sunlight in both ultraviolet regions of the spectrum: UV-A (315-400 nm) and UV-B (290-315 nm). Upon absorption of a photon PAHs undergo two photochemical processes: photosensitization and photomodification. In a photosensitization reaction, singlet-state oxygen and other active oxygen species (i.e. superoxides) are generated. During photomodification, PAHs are structurally altered to a variety of products with quinones being the most common (Inomata & Nagata 1972, Valerio et al. 1984, Huang et al. 1993, 1997a, b, Duxbury et al. 1997, McConkey et al. 1997). For example, Inomata & Nogata (1972) identified 5-phenoxy-3,4-benzo(a)pyrene, benzene and carbon disulfide along with a series of quinones as a product of the transformation of benzo(a) pyrene after exposure to a UV lamp. Similarly, Huang et al. (1997b) found that photomodification of anthracene resulted in a complex mixture of chemicals, some of which (anthroquinone, benzoic acid, phthalic acid) have been identified. Actinic (short wave) radiation present in the natural solar spectrum is more effective in promoting PAH modification than visible light (Huang et al. 1993, 1997a). The water solubility of the UV-treated PAH compounds is higher than that of non-photomodified forms and therefore not only gaseous or particle forms of PAHs can be accumulated by plants, but also compounds that are scavenged from the air by wet precipitation (Huang et al. 1997b). Because few studies on the effects of ultraviolet of light on PAHs have been conducted and that this area of research remains in its infancy, we do not recommend the use of products of photodegradation as quantitative markers of exposure to flare emissions.

Pollutant metabolites and breakdown products are occasionally more convenient to measure than the pollutant itself. The metabolic degradation of PAHs by pure cultures of a variety of bacteria, fungi and primitive algae has been documented and the biochemical pathways have been elucidated (Varanasi 1989, Cerniglia 1992). However, the amount of information available on PAH metabolism in higher plants is scarce and fragmented.

PAHs, considered as xenobiotics because of their physico-chemical nature (Connell 1990), are expected to be metabolized in a similar fashion as other xenobiotics. There are three main steps involved in the metabolism of xenobiotics (Martinoia et al. 1993). In the first step compounds are reduced or oxidized. PAH toxicity may be enhanced through these processes. This phenomenon is referred to as bio-activation. In the second step PAHs are further metabolized through conjugation with amino acids, oligopeptides or hexoses. This step of degradation of xenobiotics was confirmed to occur under exposure to airborne PAH in four species of woody plants. Nakajima et al. (1996) quantitatively measured synthesis of *β-O*-glucoside and *β-O*-glucuronide conjugates of 1-hydroxypyrene in leaves of cherry, maple, ginko and camphor plants growing at two sites near busy highways within the Tokyo metropolitan area. There were large differences in the amounts of conjugates and conjugate/pyrene ratio among species. These differences may be caused by variations in conjugation activity and enzymatic hydroxylation activity for pyrene. The authors concluded that the amounts of atmospheric PAHs scavenged by vegetation were much larger than estimates based on measurements of intact compounds in plant tissues. The ability of plants to metabolize pyrene has also been demonstrated by Huckelhoven et al. (1997). They found that in wheat about 90% of applied pyrene was transformed into a

complex mixture of carbohydrate conjugates while 1-hydroxypyrene methyl ether was the main metabolite accumulated in foxglove. The third step in the metabolism of xenobiotics involves the excretion of conjugated compounds from the cytoplasm. This is done by glutathione S-conjugate transporters, which transport toxins to the vacuole. Although conjugated PAHs might also be sequestered to vacuoles in a similar fashion, no experimental data is available.

The detailed fate of PAHs in plant systems at the cellular level needs further study. The use of metabolites as quantitative indicators of exposure to PAHs appears to be premature. Until reliable protocols for the measurement of PAH metabolites and breakdown products are developed, analysis of modified PAH compounds accumulated in plant tissues as markers of exposure to air emissions from flares is not recommended.

4. VEGETATION AS A PAH SINK

Although in terrestrial ecosystems plant biomass is believed to contribute to the global circulation and partitioning of several semivolatile organic compounds (Calamari et al. 1991), only one research group has attempted to quantitatively estimate the magnitude of vegetation as a sink for PAHs (Simonich & Hites 1994a, b, 1995). They proposed a regional mass balance of ten PAHs for the northeastern United States. This region encompasses 3.3×10^6 km^2, 70 % of which is covered by farmland and urban vegetation, 20 % is forested and 10 % is occupied by water bodies (mostly the Great Lakes). This model was developed based on their own measurements of PAH concentrations in 147 vegetation and soil samples at a suburban site in Bloomington, Indiana as well as on published values for total PAH emissions for the region and for PAH concentrations in ambient air, water, sediments and soils. Their model indicated that vegetation was an important sink for PAHs under regional conditions of the area of study (Figure 1). It was estimated that 44±18 % of the PAHs emitted into the atmosphere from local sources was removed by vegetation. Approximately 5 and 10 % of total PAHs emitted were directly deposited onto water surfaces and soil, respectively. Transformation of PAHs and their transport out of the region accounted for the remaining 41 % of the total pool. Simonich & Hites (1994a) remarked that removal rates changed depending on the season. The key factors affecting partitioning rates were ambient temperature and the surface area of vegetation. Although this model has been developed for the northeastern regions of the USA, it should be possible to apply it under Alberta conditions. We might expect that on average 40 % of emitted PAHs would be scavenged by plants with higher PAH burdens in areas adjacent to flare operations.

Because PAHs are present in both air and soil one has to consider the possible pathways of entry into plants. There are two possible pathways through which airborne PAHs can enter plants:

(i) uptake by root systems, once pollutants are deposited to the soil, and
(ii) uptake by above-ground organs, mainly leaves, directly from air.

4.1. Root uptake

According to Simonich and Hites' model (1994a), over 50 % of PAHs emitted to the atmosphere from local sources are deposited to soils either through direct deposition or from plant litter (Figure 1). Soils are major sinks of PAHs and on average, concentrations of these hydrocarbons

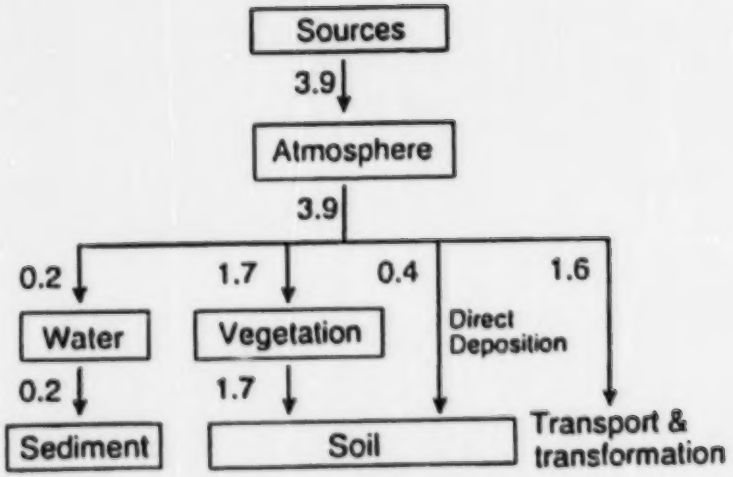

Figure 1. **Total PAHs flow rates (in 10^6 kg/year) for the Northeastern United States. (From: Simonich & Hites (1994) Nature 370, 49-51).**

are 10-100 times higher in soils than in vegetation (Grimmer 1983, Wilson & Jones 1993). Thus, substantial amounts of PAHs could be available for uptake by root systems.

A number of studies on uptake and translocation of PAHs in plants have been conducted (Edwards 1983). While a number of researchers have concluded that PAHs could be translocated from roots to shoots, this issue remains somewhat controversial. At the very least, it appears that uptake and translocation of PAHs is species- and substrate-specific. For example, Edwards et al. (1982) found that uptake of ^{14}C-anthracene from nutrient solution was 30-times greater than that from soil. It is possible that in these experiments, the ^{14}C detected in above-ground tissues was associated with break-down or metabolized products and that PAHs per se were not translocated. Durmishidze et al. (1974) (cited in Edwards 1983) found that PAHs supplied to plant roots were broken down, possibly by the plant or by microorganisms, and that the ^{14}C label was incorporated into organic acids. Recent studies on the availability of PAHs in soil cast further doubt on the possibility that translocation of PAHs from soil to shoots represents a significant contribution to the total pool of PAHs in leaves. Studies show that after entering soil systems, volatile PAH compounds may be degraded before plant uptake occurs, while heavier compounds may be bound to soil particles and soil organic matter. Therefore, their availability to plants is likely restricted. Aprill & Sims (1990) suggested that the non-ionic, non-polar structure of PAH compounds leads to partitioning out of the polar water phase and onto hydrophobic surfaces in a soil matrix. The PAHs with three or more rings tend to be strongly adsorbed to the lipophilic soil organic matter (cited in Reilley et al. 1996) or bound to the lipid components of roots. In the latter case, PAHs are virtually immobilized on the root surface and translocation of four- or more-ringed compounds to foliar portions of the plants was negligible (Sims & Overcash 1983, Thomas et al. 1984, Edwards 1988, Wild & Jones 1991).

More recent studies using soil systems have reported enhanced microbial degradation of PAHs in the rhizosphere (Cerniglia 1992, Schwab & Banks 1994, Reilley et al. 1996). Therefore, the majority of PAHs accumulated in soil is either degraded or tightly bound to soil particles, making them largely unavailable to plants. PAH-contaminated soils might contribute to higher concentrations of PAHs in plant shoots through volatilization of low molecular weight PAHs into the surrounding air at high ambient temperatures and subsequent uptake by leaves (Simonich & Hites 1994b). Thus, although more than 50 % of PAHs emitted to the atmosphere from a particular source is deposited to soils, the availability of these compounds for plant uptake by roots appears to be very low.

Based on experimental data presented in this section we do not recommend the use of plant roots, litter or soil samples as indicators of exposure to flare emissions in Alberta because PAHs in soil are either degraded by soil microorganisms or bound to soil particles leading to low availability of PAHs.

4.2. Foliar uptake and accumulation of PAHs

Recent studies show that leaves and to a certain extent other above-ground organs such as bark, fruits and stems are the main sinks of airborne PAH compounds in plants. The process of interception depends on several biotic and abiotic factors, including phase state of PAH, leaf

surface area, lipid concentration in plant tissue, octanol-air partitioning coefficient and ambient temperature.

4.2.1. Factors affecting uptake and accumulation

Phase state of PAHs

Volatile PAHs are expected to enter plant tissues primarily by gaseous diffusion via open stomata. Compounds with a vapor phase component in the air are subject to an air-leaf exchange process moving towards equilibrium over time (Tremolada et al. 1996). Compounds of intermediate volatility are also mainly subject to dry gaseous deposition. However, nonvolatile substances (six and more rings) are accumulated on plant surfaces in the form of dry, particle-bound deposition. Several experiments performed on PAHs with a wide range of vapor pressures validated these hypothetical modes of accumulation. Gaseous dry deposition has been shown to be a key process for many organic contaminants including PAHs. For example, Nakajima et al. (1995) performed simultaneous measurements of three PAH concentrations in azalea (*Rhododendron*) leaves and in surrounding air. The concentrations of non-volatile benzo[a]pyrene and perylene in the leaves were proportional to those present in particulate matter suspended in ambient air. The concentration of volatile pyrene in the leaves, however, was correlated to that in the vapor phase. Similar field studies of deposition of eleven PAH compounds onto different plant surfaces, including leaves, bark and seeds from sugar maple and white pine were carried out by Simonich and Hites (1994b). They concluded that while particle-phase PAHs were found in both tree species, the predominant pathway into tree leaves was gas-phase deposition. This observation was recently confirmed by investigations of PAH deposition in two forest canopies (Horstmann & McLachlan 1998).

At the same time, Ignesti et al. (1992) documented the importance of solid-phase PAH deposition. Air particulate levels of non-volatile benzo[a]pyrene and five other PAHs correlated with their deposition onto olive fruits growing in a heavily polluted region of Florence, Italy. Khun et al. (1998) analyzed the concentrations of thirteen PAHs in poplar leaves collected from young trees grown in the vicinity of a high volume traffic highway (60,000 vehicles per day). They presented evidences that most of the non-volatile compounds were adsorbed onto the leaf surface. Very similar findings were reported by Yang et al. (1991) who showed that PAHs with more than four rings, due to their predominant particulate form, deposited onto leaf surfaces of the grass *Eragrostis tenuifolia* growing close to an urban roadway. Tremolada et al. (1996) studied the accumulation of 16 PAHs in pine needles collected in areas of different population densities in the United Kingdom. They reported that total content of PAHs ranged from 19 to 3091 ng/g dry weight in sparsely populated areas of northern Scotland and densely populated areas of southern England, respectively. They found a wide spectrum of PAHs ranging from three-ringed anthracene to six-ringed coronene in pine needles. In most cases, however, low molecular weight phenanthrene dominated the PAH burden of the samples, being between 50 and 80% of the sum of PAHs. Based on Leahey's (1996) calculations of ground level concentrations of PAHs (Table 3) we hypothesize that phenanthrene would be extensively accumulated by plants growing in the vicinity of sour gas flares such as those in Alberta. This compound is the second most abundant in sour gas emissions (Strosher 1996) and its estimated average annual concentration in the vicinity of a flare is 11.8 ng m^{-3} (Leahey 1996).

Table 2. PAHs* accumulated in tissues of indicator plants.

Species	Location	Sample size	PAH determined	Time of sample collection	References
Laurus nobilis (Bay laurel)	15 sites throughout city of Florence – Italy	30 g of leaves	Σ 10 PAHs – up to 477 µg/kg **PHEN**, FLU, **PYR**, **B[a]P**, **CHRY**, B[b]F, **B[k]F**, B[a]A, D[ah]A, **B[ghi]P**	Leaf samples were collected in summer, fall and winter.	Lodovici et al. 1994
Laurus nobilis (Bay *laurel*)	13 cities of *different* size in Italy	10 g of *leaves*	Σ 9 PAHs – up to 880 µg/kg **FLT**, *PYR*, **B[a]P**, **CHRY**, B[b]F, **B[k]F**, B[a]A, D[ah]A, **B[ghi]P**	Leaves grown in the current year were collected.	*Lodovici* et al. 1998
Olive	34 sites in a radius of 15 km from Florence – Italy	100 g of fruits	Σ 5 *PAHs* – up to 15 µg/kg **FLT**, **PYR**, **B[a]P**, B[a]A, **B[ghi]P**	*Olive* fruits were harvested in late November.	*Ignesti* et al. 1992
Poplar	*Roadside* of a highway (60 000 vehicles per day) in Frankfurt – Germany	*100* g of leaves	Σ 13 PAHs – up to 4.2 µg/m^2 **PHEN**, FLU, **ANT**, **FLT**, **PYR**, B[a]A, **CHRY**, B[b]F, **B[a]P**, **B[k]F**, D[ah]A, **B[ghi]P**, **IP**, **COR**	*Leaves* were collected every 14 days from May 21 to until October 8.	*Khun* et al. 1998
Azalea	2 sites in Tokyo – Japan	8 g of leaves	**B[a]P** – up to 40 ng/g **PER** – up to 11 ng/g **PYR** – up to 495 ng/g	Samples were collected once a month, from June to May. Only mature leaves were harvested.	*Nakajima* et al. 1995

Species	Location	Sample size	PAH determined	Time of sample collection	References
Azalea	8 *sites* located 70-700 m from highways in Tokyo –Japan	10 g of leaves	1-NP *only* 2.5 ng/g	Data not available.	*Nakajima* et al. 1994
Pine	28 *sites* throughout the UK	10 g of needles	Σ 16 *PAHs* – up to 3,090 ng/g **PHEN**, FLU, **ANT**, **FLT**, **PYR**, **CHRY**, B[b]F, **B[a]P**, **B[k]F**, D[ah]A, D[ac]A, **B[ghi]P**, **COR**, BA, **ACE**, MPHE	*Samples* were collected in two periods: in May-June and in August.	*Tremolada* et al. 1996
Sugar *maple* White pine Corn	13 sites *in* the northeastern USA	2-5 g of leaves	Σ 16 PAHs – up to 1,600 ng/g **PHEN**, FLU, **ANT**, **FLT**, **PYR**, **CHRY**, B[b]F, **B[a]P**, **B[k]F**, **B[ghi]P**, **COR**, **ACE**, **AL**, B[a]A, RA, **B[e]P**	*Leaves* were collected on various dates over summer and fall.	*Wagrowski* & Hites 1997
Eragrostis tenuifolia (grass)	2 *locations* in Brisbane – Australia, 0.5 m from the road	200 g of leaves	Σ 4 *PAHs* – 91.1 ng/g **PHEN**, FLU, **ANT**, **PYR**	*Samples* were collected weekly during September.	*Yang* et al. 1991

Species	Location	Sample size	PAH determined	Time of sample collection	References
Grass	*Rothamsted* Experimental Station – UK	10 g of leaves or grain	Σ *16* PAHs – 4.3 – 46.6 µg/kg **FLT, PYR, CHRY,** ATT, B[b]F, **B[a]P, B[e]P, IP, B[ghi]P, COR,** B[a]A, D[ah]A, **CP[cd]P, B[ghi]F,** BNT, **TP**	*Archived* plant samples from the herbarium were studied. Grain was harvested in late August.	Jones et al. 1992
Grass	1-4.5 km from polypropylene plant	20 g *of* leaves	Σ 16 PAHs – 2,365 ng/g **PHEN,** FLU, **ANT, FLT, IP, PYR, CHRY, NAP, AL, ACE,** B[a]A, B[b]F, **B[a]P, B[k]F, B[ghi]P,** D[ah]A	*Leaf* samples were collected 48 h after a fire of 10,000 ton of polypropylene.	*Meharg* et al. 1998
Spruce/oak/ beech	2 km from *town* of Bayreuth	Bulk deposition sampling	Σ 12 *PAHs* deposition velocity – 0.05-0.73 cm/s **PHEN, FLT, IP, PYR, CHRY, COR,** B[b]F, **B[e]P, B[a]P, B[k]F, B[ghi]P,** D[ah]A	Samples *were* collected on monthly basis from May to April.	*Horstmann* & McLachlan 1998
Kale	2 *sites* in industrial town of Wittlich – Germany	10 g of leaves	Σ 14 *PAHs* – up to 536 ng/g **PHEN, FLT, FLU, IP, PYR, CHRY, ANT, ACE,** B[b]F, B[a]A, **B[a]P, AL, B[ghi]P,** D[ah]A	*Greenhouse*-grown plants were exposed to ambient air at the studied site for up 2 months in fall.	*Franzaring* et al. 1992

Species	Location	Sample size	PAH determined	Time of sample collection	References
Sphagnum ssp (Moss)	1 km *from* aluminum plant	*20* g	*FLT* - 13,000 ng/g **B[a]P** –1,130 ng/g B[b]F – 1,780 ng/g **B[k]F** – 863 ng/g **B[ghi]P** – 1,210 ng/g **IP**- 3,720 ng/g	Moss bags were exposed to ambient air in the vicinity of aluminum plant during 2 periods of 30 days in fall.	*Wegener* et al. 1992
Hypnum cupressiforme (Moss)	14 sites in Bavaria, Germany, 500m from emission station	5 g	3,4-BP – up to 53 ng/g 1,12-BPY – up to 95 ng/g **FLT** – up to 186 ng/g	*Samples* collected from May to October at 3-week intervals.	*Thomas* 1984
Racomitrium canescens (Moss) *Racomitrium lanuginosum* (Moss)	20 sites in Iceland, at least 100 m from roads and settlements	5 g (dry weight)	3,4-BP – up to 48 mg/kg 1,12-BPY – up to 33 mg/kg **FLT** – up to 38 mg/kg	*Green* parts of moss were collected in the first week of July.	*Thomas* & Schunke 1984

*-Note: PAH compounds found in flare emissions in Alberta are **bolded**.
-Abbreviations of PAHs
ACE – acenaphtalene, AL – acenaphthylene, ANT – anthracene, ATT- anthanthrene, BA – benzanthracene, B[a]A - benzo[a]anthracene, B[a]P – benzo[a]pyrene, B[b]F – benzo[b]fluoranthene, B[e]P - benzo[e]pyrene, B[ghi]F – benzo[g,h,i]fluoranthene, B[ghi]P – benzo[g,h,i]perylene, B[k]F - benzo[b]fluoranthene, BNT – benzo[b]naphtho[2,1-d]thiophene, 3,4-BP – 3,4-benzopyrene, 1,12-BPY – 1,12-benzoperylene, CHRY – chrysene, COR – coronene, CP[cd]P – cyclopenta[c,d]pyrene, D[ac]A- dibenzo[a,c]anthracene, D[ah]A- dibenzo[a,h]anthracene, FLU – fluorene, FLT – fluoranthene, IP – indeno[1,2,3-c,d]pyrene, MPHE – 1-methylphenanthrene, 1-NP – 1-nitropyrene, NAP- naphthalene, PHEN – phenanthrene, PER- perylene, PYR – pyrene, RA – retene, TP – triphenylene.

Table 3. **Largest maximum predicted ground level concentrations of PAH compounds associated with sweet and sour gas flaring. (Adapted from: Leahey 1996).**

Compound	Sweet Gas Flare		Sour Gas Flare	
	Daily Average ($ng\ m^{-3}$)	Annual Average ($ng\ m^{-3}$)	Daily Average ($ng\ m^{-3}$)	Annual Average ($ng\ m^{-3}$)
Acenaphthene	47.0	1.7	23.8	1.9
Acenaphthylene	370.0	13.5	-	-
Anthracene	671.2	24.5	-	-
Benz(a)Anthracene	272.7	9.9	-	-
Benzo(a)Pyrene	16.8	0.6	3.0	0.2
Benzo(e)Pyrene	11.7	0.4	3.0	0.2
Benzo(g,h,i)Fluoranthene	160.2	5.8	-	-
Benzo(g,h,i)Perylene	4.2	0.2	-	-
Chrysene	33.6	1.2	11.9	0.9
Coronene	1.7	0.1	-	-
Fluoranthene	818.9	29.9	62.4	4.9
Indeno(1,2,3,-cd)Pyrene	2.5	0.1	-	-
Perylene	10.1	0.4	-	-
Phenanthrene	-	-	151.6	11.8
Pyrene	509.3	18.6	371.5	29.0

Leaf surface area

Total leaf area is the most important plant feature affecting the rate of interception and accumulation of airborne PAHs. The surface area of the above-ground parts of plants exceeds by far the area that the plants grow on. Leaves account for the greatest proportion of the plant surface area, while stems and twigs generally play a secondary role. The ratio of the sum of leaf areas to the ground area in which the plants grow is called the leaf area index (LAI) (Salisbury & Ross 1992). LAI values up to eight are common for many mature crops, depending on species and planting density, but they can reach values as high as twenty (Riederer 1990). The use of the LAI also allows for comparison of accumulation rates between species.

McCardy (1994) found that rate constants normalized to plant dry weight varied between species by a factor of 50, while rate constants normalized to leaf surface area varied by only a factor of 4 suggesting that leaf area is a better parameter to use in expressing rate constants for PAH accumulation. In conifers, rate constants normalized to leaf surface area may also vary based on the technique used for their measurement. For example, Schreiber & Schonherr (1992) found that specific surface area (total surface area per unit length, used to describe area of needles having different cross-sectional shapes) varied by more than one order of magnitude between needles of different conifer species while projected needle area (the one-dimensional outline of a needle) varied only by a factor of approximately 2. This illustrates the importance of using indices that reflect total leaf area in measurements of PAH accumulation rates in conifers.

Lipid concentration

Leaves and other parts of higher plants directly exposed to the atmosphere are covered with a continuous, extracellular layer called the cuticle. The major role of this structure is the protection against passive water loss to the atmosphere (Salisbury and Ross 1992). It also determines the rates of uptake of all substances that are not able to enter the stomata by diffusion in the gas phase. The plant cuticle consists of the insoluble biopolymer cutin (mainly composed of hydroxyalkanoic acid monomers) and wax-like lipids which are deposited within the polymer layer and on the cuticle/atmosphere interphase (Poborski 1988, Reiderer 1989). Due to its chemical structure, the cuticle possesses strong lipophilic properties, affecting the accumulation of airborne PAHs. The waxy surface of leaves and often other organs like stems and fruits not only traps particulates but can also intercept vapor phase contaminants, as documented for pine needles (Kylin et al. 1994). Poborski (1988) studied the emission of naphthalene from a coking facility and suggested that due to its non-polar properties this gaseous, two ringed PAH permeated the cuticle about 300 times faster than water. The cuticle is not only a route for the uptake of atmospheric pollutants but it may also act as an accumulation compartment for persistent lipophilic chemicals like PAHs (Khun et al. 1998). The total amount of cuticlar material in temperate forests and agricultural plant communities can range from 180 to 1500 kg/ha (Sabljic et al. 1990). This means that plant species differ in the content of culicular material, which is an important characteristic with respect to the degree of PAH accumulation. The amount, composition and sorption properties of cuticle also depends on age, time of year (mainly due to ambient temperature) and overall conditions of the plant. Taking into consideration these features of the cuticle, one can expect that lipid concentrations on plant surfaces may account for differences in the amounts of accumulated PAHs. Simonich and Hites (1994b) measured concentrations of ten PAHs in leaves, bark and seeds of sugar maple and

white pine. Plant tissues contained varying amounts of lipids with pine bark being highest (170 mg/g dry wt), followed by maple bark (33 mg/g dry wt), pine needles (23 mg/g dry wt), maple leaves (16 mg/g dry wt) and maple seeds (6 mg/g dry wt). Simonich and Hites (1994b) suggested that the differences in the PAH concentrations observed between tissues could be explained by differences in lipid content. Tissues containing more lipids accumulated significantly more PAHs on a per lipid basis when exposed to the same concentrations of PAHs in air.

Until recently, the kinetics of uptake of organic compounds had been described using a one-compartment model for the entire leaf, without distinguishing between outer cuticlar and inner leaf compartments (Simonich & Hites 1995). More recent experiments in which morphological structures were considered revealed that the kinetics of leaf uptake are best explained by a two-compartment model which characterizes partitioning of PAHs to both compartments separately. Fast (days to weeks) and slow (months to years) PAH accumulation in vegetation exposed to airborne pollutants have been observed under field conditions by Simonich and Hites (1994b). They found that new vegetation accumulated PAHs quickly, within two weeks of emergence, suggesting a predominant role of the outer (fast) compartment in the process. Diffusion of surface-bound PAHs into the inner compartment is the rate-limiting step for whole leaf contamination and depends on ambient temperature and concentration of PAHs. Khun et al. (1998) presented data demonstrating the existence of two separate sinks for PAHs within poplar leaves. They investigated the partitioning of 13 PAHs between the soluble cuticlar lipids and the remaining leaf. The study showed that the majority of the PAHs were embedded near the leaf surface. Only PAHs with relatively low molecular weights absorbed by the outer compartment could penetrate into deeper leaf layers at low rates. Five- and six-ringed compounds, however, were not detected in the parenchymatic tissues during the five months of experimentation, suggesting that cuticlar material covering leaves acts as a long-term inert storage compartment for both volatile and non-volatile PAHs. It is also possible that volatile, low molecular weight PAHs found inside the leaves reached the inner compartment via gaseous diffusion through open stomata. Lodovici et al. (1998) also showed that PAHs are strongly bound to the lipophilic compartment of leaves. They tested whether a fraction of the particulate PAHs deposited on foliar surfaces of *Laurus* might be washed away during heavy rain events. Controlled rinsing with water did not modify levels of PAHs in leaves.

Octanol-air partitioning coefficient

The octanol-air partitioning coefficient (K_{oa}) is recognized as an important parameter in the understanding of sorption of airborne organic compounds by leaf surfaces. Given that K_{oa} is a measure of a compound's preference for octanol (or the plant wax) over air under equilibrium conditions, K_{oa} should be strongly related to the ratio of the concentration of lipophilic compounds measured in the plants to the concentration measured in the air. This proportion is referred to as the bioconcentration factor ($BCF_{p/a}$) (Sabljic et al. 1990, Trapp et al. 1995). The K_{oa}–based BCF has been used to predict leaf-air PAH partitioning by several authors (Simonich & Hites 1994b, 1995, Tremolada et al. 1996). For example, Tremolada et al. (1996) found that this coefficient can reliably predict air concentrations of more volatile PAHs like fluorene and phenanthrene, with log K_{oa} <8, since these compounds approach equilibrium with the gas phase. Use of this coefficient is not recommended for prediction of air concentrations of PAHs with higher molecular weights (K_{oa} – 8-12).

Ambient temperature

The partitioning of PAHs between the atmosphere and vegetation depends on ambient temperature. As a rule, at low air temperatures in fall and winter, the majority of emitted compounds are scavenged by plants, either conifers or evergreen species in warmer climatic regions. However, at high ambient temperatures in summer, few-ringed compounds may volatilize back to the atmosphere. Such seasonal fluctuations in PAH partitioning have been observed by several investigators (Ignesti et al. 1992, Franzaring et al. 1992, Lodovici et al. 1994, 1998, Simonich & Hites 1994b, Nakajima et al. 1995, Khun et al. 1998). However, temperature affects the partitioning of solid-phase PAHs to a much lesser extent. High molecular weight, multi-ringed, non-volatile PAHs have higher binding affinities to particles and therefore their accumulation in plants is not temperature dependent (Simonich & Hites 1994b).

4.2.2. Selection of suitable species as markers of exposure to flare emissions in Alberta

The data presented above provide us with relevant information regarding the selection of plant species that could be used as quantitative markers of exposure to flare emissions in Alberta. Ideally, the selected plant species should have leaves with a large surface area and the leaves should be covered with a thick, waxy cuticle. These two anatomical features are most important in the interception of PAHs from air. Longevity of leaves is also an important factor contributing to the efficiency of interception of air borne compounds. Conifer needles and evergreen leaves can accumulate PAHs over periods of months to years, whereas deciduous plant leaves will accumulate PAHs over a single growing season.

The range and distribution of a given plant species within the area where flare operations occur are also important. We suggest that lodgepole pine and canola are the best candidate species for this work. These two species are well represented throughout Alberta. For instance, the 4.5 million acres of canola cultivated in Alberta are spread from the High Prairie region in the northwest to the Medicine Hat area in the southeast. Logdepole pine is the most common and abundant tree on the eastern slopes of the Rocky Mountains and foothill regions. Leaves of both species are covered with a thick layer of cuticlar material that has a high potential for interception and preservation of non-volatile and volatile PAHs (Franzaring et al. 1992, Tremolada et al. 1996). Furthermore, pine needles, which remain on trees for at least three growing seasons, can be also used to monitor PAH accumulation from late fall to early spring when deciduous plants are leafless.

4.3. Interception of PAHs at the canopy level

Early studies by Matzner (1984) have shown that forests are effective air filters of PAHs. He estimated annual rates of total deposition of four PAHs (fluoranthene, 3.4-benzopyrene, indeno(1,2,3-cd)pyrene and 1.12 benzoperylene) using the flux balance of forest canopies of a beech and a spruce stand located in four regions (Heide, Gottingen, Harz, Solling) of Germany. The total deposition was divided into precipitation (bulk) deposition – (the gravitational deposition by rain, snow and particles) and interception deposition – (influenced by the kind and structure of the receiving surface - leaves or needles). He found that litter-fall accounted for 40 to 70 %, and 30 to 50 % of total PAH deposition under spruce and beech forests, respectively.

Differences between stands were due to differences in interception deposition because the spruce needles stay on the tree longer than do beech leaves and therefore have a longer period of PAH accumulation. This study showed that vegetation plays an essential role in the annual cycling of PAHs and absorbs substantial amounts of these pollutants from the atmosphere. An interesting extension of Matzner's research was recently reported by Horstmann and McLachlan (1998). They compared the deposition of twelve PAHs (phenanthrene, pyrene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, coronene, benzo[ghi]perylene, dibenz[a,h]anthracene, fluoranthene, benzo[k]fluoranthene, indeno(1,2,3-cd)pyrene, chrysene) onto a coniferous and a deciduous forest canopy. In addition, ambient air was sampled continuously, with separate analysis of the gaseous and particle-bound phases. The gaseous deposition velocities were 0.78 cm s^{-1} for spruce and 3.6 cm s^{-1} for oak and beech stands. These values are high compared to deposition velocities that have been measured for inorganic gases, reflecting the fact that lipophilic organic chemicals are taken up by the leaf cuticle and not just via the stomata. Since the dry particle-bound deposition velocities were considerably lower (0.05 and 0.73 cm s^{-1}, for coniferous and deciduous canopies, respectively), they underscored the importance of gaseous deposition in the partitioning of PAHs to forest ecosystems.

The results presented above may have some application in the measurement of PAH accumulation in plants in Alberta. Similarities in climatic and floristic conditions between Germany and Alberta suggest the possibility of using spruce and possibly beech as marker species of exposure. Additionally, several PAHs examined in the German studies (phenanthrene, pyrene, benzo[e]pyrene, benzo[a]pyrene, coronene, benzo[ghi]perylene, fluoranthene, indeno(1,2,3-cd)pyrene, chrysene) have been found in emissions from Alberta's flares (Table 1, Strosher 1996).

5. VEGETATION AS A MARKER OF EXPOSURE TO PAH EMISSIONS

Accumulation of organic airborne compounds in vegetation has been successfully employed as a marker of exposure to emissions from urban areas, heavily polluted industrial regions and large scale industrial fires. In the past decade, many studies making use of plants as markers of PAH exposure have been reported. Table 2 serves as a summary of recent efforts in the monitoring of PAHs using plants. The main advantage of using plants as markers of exposure comes from the fact that vegetation acts as a natural "air sampler", with accumulation of PAHs occurring over time. It may be also more cost effective to collect plant tissue samples than air samples, especially in remote locations. After harvest, plant specimens can be stored frozen in the laboratory for several days until analysis using GC/MS or HPLC without any significant losses of PAHs from the samples (Thomas & Schunke 1984, Ignesti et al. 1992, Lodovici et al. 1994).

5.1. Phytomonitoring techniques

A wide variety of plant species including lichens, mosses, algae and trees have been used to evaluate the accumulation of PAHs in the environment. Plants selected for monitoring of ambient air should possess features that maximize interception of PAHs. These include high leaf area index and high lipid content in the tissue selected for sampling. Additionally, they need to

be commonly found in the study area, facilitating the comparison between individual monitoring sites within the study area. Two basic strategies can be employed in biomonitoring studies: active and passive monitoring. Active monitoring refers to a process in which plants have been grown in an artificial environment, without previous contact with a pollutant of interest. Such "clean" plants are subsequently transferred to the monitored site and exposed to the actual environment over a given time before laboratory analysis. The main advantage of active monitoring is that this method can be standardized to a high degree and that time-dependent factors can be recognized. The active approach can also be used to compare sites that do not have useful phytomonitors in common. Passive monitoring relies on analysis of pollutant content in plants collected from their natural habitat.

Active monitoring studies were conducted by Franzaring et al. (1992) who used kale (*Brassica oleracea*) for active monitoring of PAH emissions in a partly industrialized medium-sized town in Germany. Greenhouse-grown plants were distributed throughout the town and after 2 months of exposure to ambient air the accumulation of 14 PAHs (acenaphthene, benz[a]anthracene, acenaphthylene, anthracene, benzo[a]pyrene, benzo[ghi]fluoranthene, benzo[f]anthracene, dibenz[a,h]anthracene, fluoranthene, fluorene, chrysene, phenanthrene, pyrene, indeno(1,2,3-cd)pyrene) was studied. Cluster analyses of the obtained PAH profiles identified and classified the extent to which particular combustion sources contributed to the emissions found at a sampling site. Species of the genus *Brassica spp.* appeared to be useful as markers of exposure to PAH emissions and should be considered in designing monitoring protocols from flare emissions in Alberta. Given the abundance of canola (*B. napus* and *B. rapa* - members of the same plant family as kale) we recommend its use as a quantitative marker of exposure to flare operations located on agricultural lands in Alberta.

Wegenger et al. (1992) used moss (*Sphagnum* ssp) bags to monitor emissions from a plant manufacturing electrodes for the production of aluminum. Twenty grams of moss collected from a rural location of Ireland were placed into nylon hairnets and exposed for two periods of 30 days each to ambient air at a distance of 1 km from the factory. After harvest, moss samples were extracted with acetonitrile in a Soxhlet apparatus. The extracts were then concentrated and analyzed for PAH content by liquid chromatography. They found that the concentration of six PAHs (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, fluoranthene, indeno(1,2,3-cd)pyrene) in the vicinity of the factory was 30 times higher than in rural locations. The authors concluded that active air monitoring with a network of moss bags could facilitate the evaluation of PAH distribution over time and space, and can identify the emissions of PAHs by point sources. Mosses are particularly useful for active monitoring due to their large surface area, high capacity to absorb large organic molecules and their ability obtain water and nutrients from the air. Thomas (1986) compared the abilities of moss to intercept air borne PAH. He studied the accumulation of fluoranthene in a moss (*Hypnum cupressiforme)*, a lichen *(Cladonia rangiferina*) and in higher plants (*Deschampsia flexuosa, Juniperus communis, Calluna vulgaris and Pinus sylvestris*) collected in the vicinity of petrochemical facilities in Sweden. He found that concentrations of PAHs in mosses were 4 to 8 times higher than in the conifer species.

The information found in the literature suggests that active monitoring by means of moss bags may be a feasible technique for use in the case of flare emissions in Alberta. For the purpose of

active monitoring, we recommend the moss *Sphagnum fuscum,* collected from a bog in the vicinity of Perryvale, Alberta. To the best of our knowledge, no major emitters of air borne PAHs are located within a radius of 15-20 km from this site (Thormann 1999, personal communication). Since the use of mosses as markers of exposure allows for direct comparison of individual flare operations surrounded by different vegetation types, this approach should be considered as a supplement to passive monitoring.

While active monitoring has several advantages, the majority of published studies are based on a passive monitoring approach. Under certain circumstances analysis of content of the compound of interest in plants collected from their natural habitat is more convenient to perform or, in most cases, better reflects the long-term accumulation of persistent trace pollutants.

The majority of flare operations in Alberta are located in rural areas, surrounded by either perennial (forests, pastures) or annual (arable land) vegetation. Based on the literature reviewed in this report we recommend that passive monitoring using canola and lodgepole pine should be the principal technique for the investigation of the use of PAH accumulation as a marker of exposure to flare emissions.

5.2. Sampling location and atmospheric conditions

Low levels of compounds occurring in air over long periods of time can be monitored using plants. As summarized in Table 2, measurements of PAH accumulation in plants have been taken at various distances from the source ranging from 0.5 m to 4.5 km from a highway and an industrial fire, respectively. Usually, concentrations of airborne PAHs have been measured at a distance of approximately 1 km from major industrial sources (Thrane 1987, Wegenger et al. 1992). The most comprehensive analysis of the effects of distance on PAH accumulation in vegetation was published by Meharg et al. (1998). They analyzed the accumulation of 16 PAHs (naphthalene, acenaphthene, acenaphthylene, anthracene, fluoranthene, fluorene, phenanthrene, pyrene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[a]anthracene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene) in grass shoots collected at different distances (1 to 4.5 km) from the site of a nine hour long, large-scale chemical fire involving 10,000 tons of polypropylene. In their studies they took into consideration atmospheric conditions like surface wind speed, average mixed layer wind speed, temperature, humidity, and designed sampling protocols accordingly. The highest PAH concentration was observed at a sampling point located 3.2 km from the source, while at a site located at 3.0 km the concentration was 10 times lower (close to background level). Concentrations of PAHs at sampling points beyond 3.2 km declined gradually, but still remained elevated up to 4.5 km away. The authors concluded that this pattern suggests that gaseous PAH vapors arising from the fire (a very hot source) were not grounding in significant quantities until a distance of 3.2 km from the source. They suggested that PAHs with high affinities for the particulate phase were poorly intercepted by vegetation during the short fire event and PAHs in vapor phase predominantly partitioned into grass tissues.

Atmospheric conditions and sampling distance of plant specimens should be considered in the case of flare emissions. Based on PAH concentrations (mg m^{-3}) measured in a plume adjacent to and downwind from the top of two operating gas flare stacks (one sweet and one sour) Leahey

(1996) estimated ground level concentrations of 15 representative PAH compounds (Table 3) using a plume dispersion model. He predicted that the maximum daily average ground level concentration of PAHs associated with sweet gas flaring should occur within a few hundred meters from the flare. Concentrations initially decrease rapidly with distance and are about 20 % of the over all maximum concentration at distances of about 3 km from the stack. The area influenced by sour gas flare is much smaller since emissions from this stack were lower by an order of magnitude compared to sweet gas operation. High PAH concentrations are also very localized and decline to 20% of their maximum distance beyond 1.5 km from the flare. Using wind rose information collected at the Edmonton International Airport he predicted that the majority of the PAHs emitted from both sweet and sour gas flares would lie along a general NW-SE axis. Leahey's simulation also shows that most of the predicted annual average concentrations of seven PAHs associated with the sour gas flare are comparable to or greater than concentrations of the same PAHs emitted by sweet gas flare (Table 3). The largest maximum predicted annual ground level concentrations of three out of 15 PAHs are substantially higher than others. In emissions from sweet gas flare fluoranthene, anthracene and pyrene are expected to be found at concentrations of approximately 30, 25 and 19 ng m^{-3}, respectively. Pyrene, phenanthrene and fluoranthene should dominate in emissions from sour gas flare at concentrations approximately 29, 12 and 5 ng m^{-3}, respectively. These data suggest that two sets of PAHs consisting of three of the most abundant compounds should be used in field experiments depending on whether the flare consists of sweet or sour gas. We recommend that the accumulation of three-ringed anthracene and four-ringed pyrene and fluoranthene in plant tissues be studied in the case of sweet gas flares, while the accumulation of three-ringed phenanthrene and four-ringed pyrene and fluoranthene be analyzed in the case of sour gas emissions.

5.3. Correlation between concentrations of PAHs in plant tissues and air

The reliability of plants as indicators of PAH exposure is an important issue. The question that needs to be asked is: to what extent does the amount and chemical composition of PAHs accumulated in plants reflect anthropogenic activities in the study area? Convincing results validating the use of vegetation as surrogate air samplers have been presented by Lodovici et al. (1998) (Figure 2). Leaves of the evergreen tree *Laurus nobilis* that were produced within the study season were collected in late summer and in the following winter from 13 urban locations in Italy. Simultaneously, air samples were obtained from the sites of leaf collection using PTFE filter to collect the particulate fraction and ORBO 43 sorbent tubes containing 50 mg of washed XAD-2 resin to adsorb volatile PAHs. The pump was set at 6 L/min and 6 h samples were repeated for four consecutive days with similar weather conditions. The authors found a high correlation ($r=0.824$) between carcinogenic PAH levels in air samples and those in leaves.

The same researches investigated the accumulation of lead in leaves of *Laurus* from 15 sites located in downtown and suburban areas of Florence, Italy (Lodovici et al. 1994). They observed that tissue concentrations of lead measured by atomic absorption technique were significantly higher in leaf samples from the downtown region with high traffic volume of automobiles powered by leaded gasoline. Interestingly, the concentration of lead was highly correlated ($r=0.829$) with the total concentration of 10 PAHs measured in *Laurus* leaves (Figure 3). This finding suggests that it is possible to use PAH accumulation as a surrogate measure of exposure

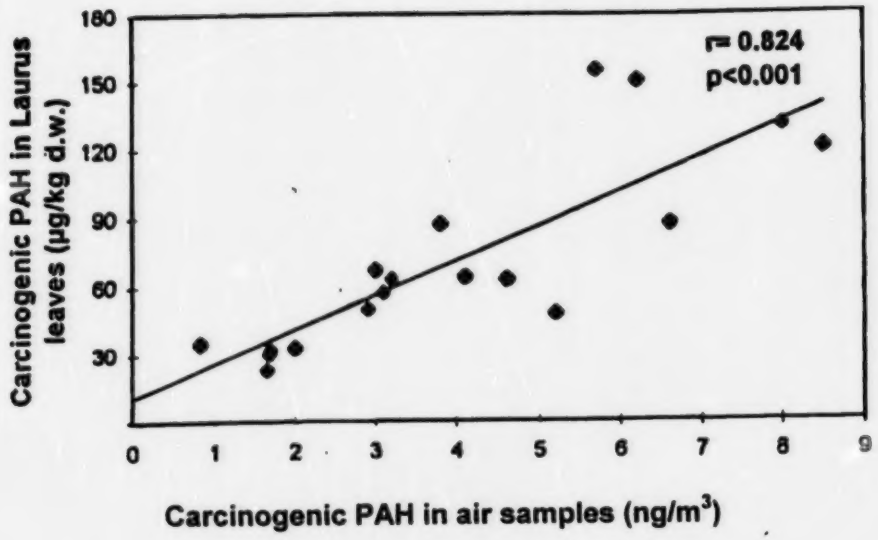

Figure 2. **Correlation between the carcinogenic PAH levels in air samples and the carcinogenic PAH [benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)fluoranthene, and chrysene] concentrations in *Laurus* leaves collected concurrently from several polluted sites in cities of Tuscany, Italy. Each value of air PAH level is the mean of 4 samplings (6 h each) obtained in four consecutive days. Leaves grown for one vegetation season were collected. (From: Lodovici et al. (1998) Chemosphere 36, 1703-1712).**

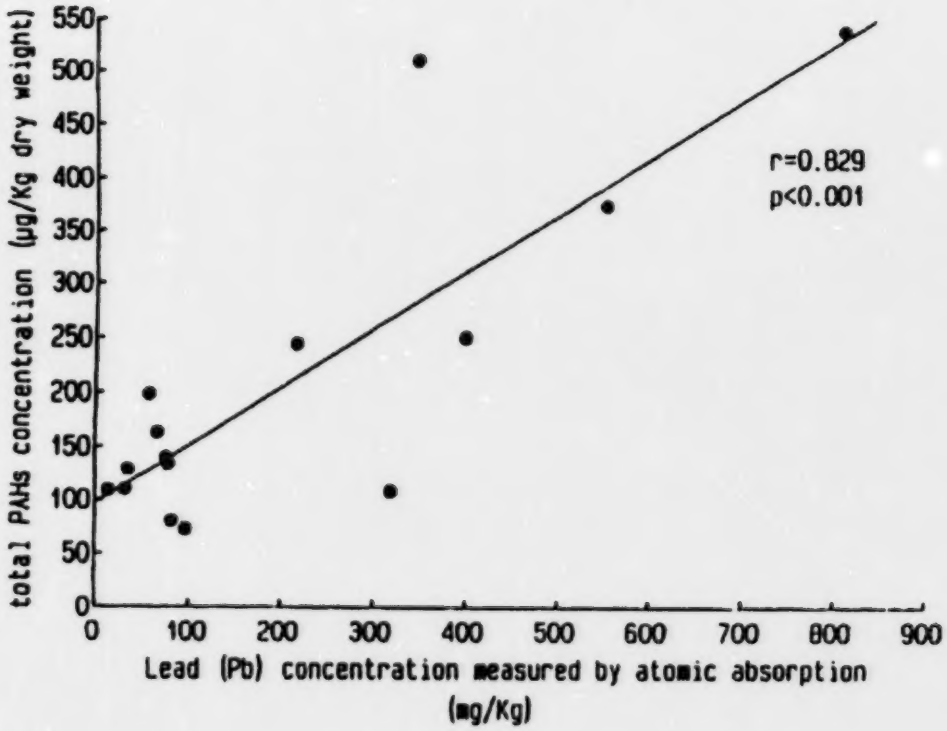

Figure 3. **Correlation between the total PAH concentration [phenanthrene, fluorene, pyrene, benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(a,h)fluoranthene, and chrysene] and lead (Pb) concentration in *Laurus* leaves collected from 15 sites of different traffic volume in the Florence area, Italy. Leaves grown for one vegetation season were collected. (From: Lodovici et al. (1994) Sci. Total Environm. 153, 61-68).**

to flare emissions containing PAHs and other types of compounds, for instance sulfur derivatives in Alberta. This study will likely encourage the scientific community to further explore the potential use of plants as biomarkers for the measurement of PAH emissions from various sources.

6. CONCLUSIONS AND RECOMMENDATIONS

Several species of plants have been shown to accumulate airborne PAHs. Accumulation appears to be a reliable quantitative marker of exposure to emissions from urban areas, industrial facilities and other operations where combustion of fossil fuels is involved. Concentrations of PAHs in ambient air highly correlate with their concentrations in plant tissues.

Based upon the literature we recommend the use of PAH accumulation in plant tissues as a marker of exposure to air emissions from oil and gas flares in Alberta.
Specific recommendations are as follows:

1. The principal technique should be passive monitoring performed in natural habitats surrounding flare operations. Given their wide distribution throughout Alberta, lodgepole pine and canola should be used as marker species for exposure to air emissions from oil and gas flares in the province. Additionally, active phytomonitoring using Alberta-grown moss (*Sphagnum fusca)* should be performed, to compare emissions from flare operations where no natural species are in common.

2. Needles of lodgepole pine should be harvested in March before the start of the vegetation season, to reflect accumulation of PAHs in winter. Newly developed needles should be sampled in September to reflect accumulation of PAHs throughout the summer months. Leaves of canola should be harvested in July, giving approximately 2-month exposures to emissions. *Sphagnum* bags placed in plastic hairnets at 1 m above ground level in the vicinity of flare operation should be used to obtain temporally resolved data on accumulation of PAHs. Samples should be collected up to 5 times throughout the vegetation season (May-September) at 3-week intervals.

3. Based on a limited amount of information on plume dispersion and estimated ground level concentrations of PAHs we suggest that in central Alberta plant leaves should be sampled at a distance of 500 m either to the NW or the SE of the flare where annual average ground level concentrations of PAH are predicted to reach their maxima. We also recommend that sampling distances and directions be experimentally verified. In other parts of the province the direction of the sampling locations should be chosen based on meteorological information obtained from local airports.

4. Anthracene, pyrene and fluoranthene contents of plant tissues should be analyzed from the areas adjacent to sweet gas flaring, while phenanthrene, pyrene and fluoranthene contents of plant tissues from areas surrounding sour gas operations should be analyzed. These two sets of PAHs consist of compounds which partition to both gaseous (three ringed) and mainly particle (four-ringed) phases thus facilitating monitoring efforts.

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